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ACOUSTIC EMISSIONS DURING HYDRIDE FORMATION*

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ABSTRACT

When a metal or alloy forms a hydride, the phase change is usually accompanied by the release of acoustic energy. The density changes that accompany hydride formation may also produce cracking and flaking. The acoustic emission accompanying these processes has been used to follow hydriding reactions and the technique has proven to be sensitive in the detection of boundaries on phase diagrams. Acoustic emission has been used to survey the hydriding properties of a number of alloys and metals (FeTi, LaNi₅, UAl₂, and Nb). This technique has proven useful as a method for monitoring particle breakup and for identifying laboratory procedures necessary to activate the hydride.

INTRODUCTION

Acoustic emission is rapidly becoming a standard technique in non-destructive testing. It has also been used as a research tool in investigating structural changes and phase transformations in solids [1-5]. In general acoustic emission appears to be produced by phase transformations of the martensitic or displacive type. The detectability of such emissions is apparently determined by the volume of the crystal which simultaneously transforms. During the formation of a metal hydride, emission can be produced by both the phase transformation itself and by cracking of the material due to volume changes. This is dramatically shown by a film of the reaction of LaNi₅ with hydrogen produced by the Philips Research Laboratory [6]. In this film an acoustic transducer was coupled to the reacting alloy and a sound tract added to the film. This sound tract is typical of the type of noise heard in the audio monitor of an acoustic emission test.

In this paper we have used commercially available acoustic emission equipment to explore the emission produced during the reaction with hydrogen of the metals LaNi₅, FeTi, Nb and UAl₅. Our results show the value of acoustic emission in both detecting phase changes in metals during ~~hydration~~ and in monitoring the progress of the hydriding reaction. — hydriding

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EXPERIMENTAL

Apparatus

The 316 stainless steel Seiverts apparatus used in the hydriding reactions was capable of attaining pressures up to ~~70.0~~ MPa (10000 psi) of hydrogen and was designed with a manifold containing a series of pressure transducers and calibrated volumes. Both hydriding and dehydriding processes were studied and although the uncertainty in stoichiometry varied with sample temperature and hydrogen to metal ratios, the error is estimated to be less than $\pm 5\%$. The hydrogen was purified by passing it through a uranium hydride column located at the inlet to the reactor system. The acoustic emission was detected by means of a Dunegan/Endevco SIMB transducer for measurements under 100°C and a 1.0 MHz lead metaniobate disk in a stainless steel holder for measurements above 100°C . To minimize the effects of ferroelectric Barkhausen noise in the transducers, measurements reported here were made under isothermal conditions. Early measurements were made by coupling the transducer to the reactor with dental cement, but later it was found that silicone vacuum grease was adequate and the transducer was simply retained with spring clamps. The transducer signal was initially amplified with an Acoustic Emission Technology preamplifier (Model 160). The signal was then fed to a Dunegan/Endevco totalizer (Model 301). The preamplifier had a band pass of 0.125 to 2.0 MHz and the total gain of the system was 95 db with a one volt counting threshold. All data was taken in the summation (total ring down count) mode. In these initial experiments, no effort was made to optimize the acoustic coupling between the sample and the acoustic transducer, therefore, comparisons between the total count seen on different runs or in different samples must be made carefully. As the samples were repeatedly cycled, there was a tendency to fracture or even powder the sample. These powdered samples exhibit poor acoustical coupling. Most of the emissions detected were in the 100 to 200 KHz frequency band, a range in which the transducers were highly sensitive. By using a high pass filter, the detection of background laboratory noise was minimized and the signal gain was increased accordingly.

69 MPa
ONE
SIMB

Materials

Matheson (99.999%) Gold Seal hydrogen was scrubbed by a uranium hydride column just before it entered the reactor. The samples to be hydrided typically weighed between 5 and 10 grams. The niobium sample was in the form of a rod 6mm in diameter and was obtained from Materials Research Corporation (MARZ grade). The LaNi_5 and FeTi were made by Battelle, Columbus, and after characterization, irregularly shaped pieces 2 to 5mm on a side were broken from the ingot and placed in the reactors. The UAl_2 sample was made at Sandia Laboratories by arc melting materials whose purities exceeded 99.99%. Granular pieces of this alloy could be pyrophoric if abraded in air and therefore appropriate caution was used to minimize contamination. Pieces of the UAl_2 sample that were loaded into the reactor were between 2 and 5mm on a side.

Procedure

Typically an aliquot of hydrogen was carefully admitted to the sample chamber. The hydrogen uptake, as indicated by the gas pressure, and the acoustic emission count was recorded. The next aliquot was withheld until the reaction was estimated to have proceeded to at least 90% completion. Thus, as a series of aliquots of hydrogen were added to the sample, the cumulative acoustic emission counts were recorded as a function of the reaction time and the stoichiometry was calculated as the reaction went to completion. Subsequently, it was possible to obtain the derivative of this function, that is, the rate of change of acoustic emission with changes in composition (i.e., $\Delta E/\Delta(H/M)$ to be denoted as dE/dX). An analogous procedure was used to examine the dehydriding process.

RESULTS

FeTi

The initial experiments were performed on a large FeTi reservoir (~1100 grams), but as more experience was obtained, samples as small as 5 to 10 grams were used. During a hydriding reaction the smaller samples easily produced total acoustic emissions between 50,000 (77°C) and 140,000 (22°C) counts and structure was resolvable in the graph of total emissions vs. composition (Figure 1). The derivative of this function vs. stoichiometry (Figure 2) accentuates the structure and a number of features appear to correlate with the phase diagram proposed by Reilly and Wiswall [7]. For example, the α to $\alpha + \gamma$ phase boundary is found to coincide with a sudden decrease in emissions on both absorption as well as desorption. Samples of FeTi which were hydrided for the first time exhibited an incubation period followed by an accelerating hydriding rate followed by a decrease in rate. The incubation period was 3-4 hours long when the sample was at 27°C with an initial overpressure of 5 MPa (750 psi). This period was characterized by a very slow decrease in hydrogen overpressure. However, the acoustic activity of the sample was easily measurable and provided a more sensitive method of determining the end of the incubation period than did the pressure decrease. The subsequent accelerating reaction was easily followed both by pressure decrease and acoustic emission. In the final stage the reaction slowed considerably even though the overpressure was significantly above the equilibrium value, and again the reaction could more easily be detected using acoustic emissions than pressure changes over the sample.

The sample was dehydrided by lowering the hydrogen pressure to less than 6 Pa (50 millitorr) and raising the temperature to ~120°C. As the sample was exposed to hydrogen the second time at 27°C, the hydrogen was rapidly consumed with no incubation time and the acoustic emission was significantly suppressed until the apparent stoichiometry achieved in the last reaction was approached. Then there was a continuous increase in emissions, although the total count never reached the values that were obtained during the initial hydriding reaction. Again the hydriding reaction was observed

to slow down as the stoichiometry increased and the hydrogen overpressure decreased. Acoustic emission was observed in dehydriding as well as hydriding portions of the cycle although the total counts during dehydriding were consistently less than those observed on hydriding. After a number of hydriding cycles the FeTi particles were reduced in size such that they resembled coarse sand (~1.0 - 0.1mm diameter particles). Occasionally one of the large particles did not fracture into smaller particles, but had many cracks and crushed easily.

LaNi₅

After a number of hydriding and dehydriding cycles the total count recorded during a hydriding cycle for LaNi₅ (Figure 3) was still approximately two orders of magnitude greater than that from FeTi. It was also observed that the number of counts (3.4×10^5) on desorption were nearly identical to those on hydriding for a given temperature even though the absorption values varied strongly with temperature.

The boundaries of the phase diagram appear well defined in both absorption and desorption experiments and are indicated by sharp dips in the derivative of acoustic emission vs. stoichiometry (Figure 4). These values correspond well with breaks in the pressure-composition isotherms observed by Kuijpers and van Mal [8] although the equilibrium dissociation pressures in the current experiments were slightly higher. It should be noted that there are significant differences between LaNi₅ and FeTi in the particle sizes after several hydriding cycles. The LaNi₅ became a fine powder and the particles approached 1 micron in size on the average.

UAl₂

The UAl₂ alloy has a laves phase structure isomorphic with MgCu₂ [9]. Other compounds with this structure such as ZrFe₂ and ZrCo₂ are known to form hydrides [10]. When UAl₂ was first exposed to hydrogen an initial burst of acoustic emission indicated that the hydrogen gas had affected the alloy although the hydrogen uptake was minimal. Subsequent thermal cycling to 300°C and pressure cycling to 30 MPa (5000 psi) produced no further acoustic emission or hydrogen uptake. The sensitivity of acoustic emission to the hydriding reactions allowed us to quickly conclude that very little hydrogen was being absorbed by the alloy under the pressure and temperature conditions attainable; therefore, further studies of UAl₂ were discontinued.

Nb

The total counts recorded in forming niobium dihydride were comparable to those observed in hydriding LaNi₅. Again, abrupt changes in the slope of dE/dX vs. H/M (Figure 5) correspond well with the phase boundaries from other studies of the niobium-hydrogen system [11]. The pressure-temperature composition studies covered the transition from the α -niobium metal phase to the β -niobium hydride and then the subsequent transition from β -niobium

hydride to γ -niobium hydride. The two-phase regions are characterized by a monotonically increasing function of dE/dX vs. H/M . The niobium resembled FeTi in particle sizes after repeated hydriding cycles. The initial rod was highly cracked and brittle with occasional particles spalled off.

DISCUSSION

Acoustic emission during hydriding and dehydriding appear to originate from several different sources depending on the hydride and the processes that are occurring in a given portion of a reaction cycle. For a specified amplifier gain and detection limit, the summation mode yielded large variations between the total acoustic emission from the initial and subsequent hydriding cycles of iron titanium. The higher initial count rates can be correlated with particle fracturing that accompanies most hydriding. Because the summation mode equates single large pulses with many smaller pulses, the gross cracking and fracturing processes that occur in the initial hydriding result in a much higher total acoustic emission count than is found in subsequent cycles. The fact that after repeated cycling the emissions reach a new, but lower total count and that they do not disappear altogether makes this experimental method useful in examining other physical changes that are occurring in the samples as the reactions proceed.

Phase transformations in the niobium-hydrogen system were studied by Rashid and Scott [12] and they observed that hydride formation in niobium exhibited characteristics of both martensitic and bainitic transformations as well as classical nucleation and growth types. Briefly, they proposed a mechanism in which hydrogen atoms concentrate in the stress fields associated with defects such as dislocations. The hydrogen-metal ratios are increased to the level where the hydride is the thermodynamically stable phase and nucleation occurs rapidly accompanied by a characteristic shear. Subsequent hydrogen enrichment of the lattice in the stress fields results in a repetition of the process. That is, the progress of hydriding is not solely a diffusion limited process, but an interaction between hydrogen diffusion, nucleating sites and lattice stress fields.

Although the acoustic emission we have observed from the niobium-hydrogen system is not a conclusive test for Rashid and Scott's model, the emissions are consistent with the model. When the first increment of hydrogen diffuses into the sample there is a small series of emissions possibly associated with dislocation motions as residual stresses are relieved [13,14,15]. Little further emission is detected until the $\alpha + \beta$ phase boundary is reached after which the emissions increase monotonically as the $\alpha + \beta/\beta$ phase boundary is approached. Rashid and Scott's model of hydride formation by a series of martensitic transformations of the metal lattice with the accompanying stress waves agrees with onset of emission at the phase boundary. The emissions suddenly decrease as the $\alpha + \beta/\beta$ boundary is crossed and not until the $\beta/\beta + \gamma$ boundary is crossed is there an appreciable increase again. Rashid and Scott did not address the higher hydrides of niobium, but in this second two phase region the slope

of the function dE/dX and the nature of the emissions compare well with the $\alpha + \beta$ two phase region. The similarity of the two regions in the acoustic emission curve suggests the processes for forming the γ phase may be similar to those for forming the β phase.

The mechanisms for the emission during hydriding of LaNi_5 are less clear since less is known about the detailed microstructure on hydriding. Kuijpers and van Mal observed that the hexagonal symmetry of the lattice (CaCu_5 structure type) is preserved in the hydride [8]. However, they noted significant differences in the densities. Even without a martensitic transformation, the stress fields produced ahead of the new phase may result in dislocation motion, sudden movements of dislocation tangles and breakaway of dislocation pileups, all of which have been proposed as emission sources for a number of other materials [13,14,15]. These processes would be expected to accelerate at the $\alpha/\alpha + \beta$ phase boundary, continue across the two phase region, and diminish at the $\alpha + \beta/\beta$ phase boundary thus giving an emission signature like that observed when hydriding LaNi_5 . space

Reilly and Wiswall determined that FeTi , a bcc structure, converts first to a tetragonal structure (FeTiH) and then to a cubic structure (FeTiH_2) [7]. The alterations in the sample morphology when hydriding FeTi are significantly less than in LaNi_5 and the acoustic emission is correspondingly less. The densities before and after hydriding these alloys are in Table I. The hydriding of LaNi_5 would be expected to produce greater total stresses than the reaction with FeTi . If the emissions are assumed to be proportional to the stresses and the damping and coupling processes are comparable, the emission from LaNi_5 would be predicted to exceed that from FeTi in agreement with the observed results. Further experiments with other materials are needed to confirm this correlation.

CONCLUSIONS

Acoustic emission has been detected during all hydriding reactions examined (Nb , FeTi , LaNi_5). There appears to be more than one origin of this emission and changes in the amount of emission were found to occur at phase boundaries. The acoustic pulses associated with cracking and fracturing dominate the emissions on the first exposure of an iron titanium sample to hydrogen, but after several cycles the total count approaches a non-zero value which appears to be temperature dependent. The emission is found both on absorption of hydrogen as well as desorption; however, the desorption total count values were consistently equal to or less than the absorption values.

The emission during the hydriding of niobium is consistent with the model for phase transformations proposed by Rashid and Scott. The sources of the emission from FeTi and LaNi_5 are less clear, although the total counts correlate well with the stress fields induced on hydriding. FeTi

Acoustic emission has been found to be a useful source of information to supplement conventional methods of analyses. The emission can be used to sense the progress of the hydriding reaction such as in screening alloys at higher pressures and to detect phase changes in alloys during reactions.

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TABLE I

<u>Material</u>	<u>Density (g/ml)</u>	<u>Percent Change</u>
LaNi_5	8.3	
$\text{LaNi}_{5.6.7}\text{H}$	6.3	24
FeTi	6.5	
FeTiH	5.9	9
$\text{FeTiH}_{1.74}$	5.5	15
Nb	8.4	
$\text{NbH}_{.8}$	7.6	10
$\text{NbH}_{1.96}$	6.7	20

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5